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Synthesis and Characterization of Multi-walled Carbon Nanotube from Pine Oil and Their Impact on Carbon Fiber Reinforced Epoxy Hybrid Nanocomposite

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ABSTRACT

Synthesis and characterization of MWCNTs from used natural precursor of Pine oil & catalytic supported materials by spray pyrolysis method. This study also includes impact of MWCNTs on carbon fiber reinforced epoxy hybrid Nano composite. MWCNTs prepared over Fe, Co & Mo as catalytic support on Silica with Pine oil at three various temperatures. Characterization studies such as SEM, HR-TEM, RAMAN taken for prepared MWCNTs using Pine oil at three different temperatures 550°C, 650°C & 750°C above studies clearly shows that MWCNTs has good morphology and well-graphitization at 650°C with better yield. Also investicate the mechanical properties such as Tensile strength and modulus, Flexural strength and modulus of MWCNTs filled and unfilled carbon fiber reinforced epoxy hybrid Nano composites. Thermal properties are studied by using Thermo gravimetric analysis (TGA) for various wt. % of MWCNTs. Water absorption & chemical resistance tests also taken for MWCNTs composite material to know the capability of resistance in water absorption and chemicals. The findings of this study encourage MWCNTs & their composite materials may be used to several areas with high efficiency.

Keywords: Multi-Walled Carbon Nanotube; Pine Oil; MWNTs/Carbon composite material.

1. INTRODUCTION

Carbon has various allotropes, or multiple forms in which it occurs. The discovery of a growing number of new materials is prepared using nanotechnology. The newly-discovered Carbon nanotubes (CNTs) are one of the most important components of the nanotechnology. The Carbon Nanotubes are referred to as a highly graphitic structure with the orientation of the basal carbon planes parallel to the tube axis, whereas CNFs are the structures with the other orientations of the graphitic lamella that will leave a smaller or no central channel (Vander Wal *et al.* 2001). CNTs are prepared by commonly three methods Arc discharge, Laser ablation and Chemical vapour deposition (CVD). Kroto et al. (1985) made an important contribution to carbon nanotube research by discovering a wide family of all carbon compounds known as fullerenes. Iijima (1991) discovered the carbon nanotube (CNT) while searching for novel carbon structures; CNTs are formed on graphite cathode surfaces during the electric-arc discharge process, which is frequently used to produce fullerene powder. Filamentous carbons without or with insignificant central channel are denoted as "CNFs", regardless of their graphitic structure reported by several authors (Pérez-Cabero *et al.* 2004; Pan *et al.* 2004).

Recently carbon nanotube and graphene are used in effective electrodes in super capacitors due to their specific surface area, excellent electrical and mechanical properties (Chen *et al.* 2013). Thermal expansion of Carbon Nanotubes This may be beneficial for carbon-carbon composites. Interesting to note that in multi-walled carbon nanotubes only the outer shell participates in electrical conduction (Frank *et al.* 1998) and electrons can move between adjacent shells only by tunnelling. Difficult occur to prove the covalent attachment of molecular species to fully sp^2-bonded carbon atoms on the nanotube sidewalls. Therefore, nanotubes can be considered as usually chemically inert (Lordi *et al.* 2000; Thillaikkarasi *et al.* 2020).

It is expected that low-defect CNTs will have very low coefficients of thermal expansion (Pop *et al.* 2006). Compared with other Properties such as mechanical, electrical, electrochemical properties of the carbon nanotubes are have several practical uses and well established.

The present analysis, reveal to synthesis of one dimensional carbon nanomaterials from pine oil fraction. Followed by multi-walled filled carbon fiber reinforced epoxy hybrid nanocomposites are prepared by hand laying process on the laboratory scale. The mechanical properties in terms of tensile strength and tensile modulus, flexural strength and flexural modulus, thermal characteristic studies using (TGA) as well as water absorption behaviour and chemical resistance properties

are investigated and reported as per American Society for Testing Materials (ASTM) standard. Morphological structure of as-grown Multi-walled carbon nanotube characterised by SEM and HR-TEM & RAMAN. Thermal properties of carbon composite material analysed by TGA method.

2. MATERIALS AND METHODS

2.1 Preparation of MWNTs

The Fe-Co-Mo catalysts (0.5g) were put in the quartz boat and inserted into the middle of a quartz tube that was placed in the electrical heating furnace. To remove air and produce a nitrogen environment, the reaction furnace was run through with the carrier gas nitrogen (200 mL min-1). The temperature was increased from room temperature to 550°C - 750°C, which is the ideal temperature for MWNT growth. The carbon precursor Pine oil was then sprayed into the quartz tube at a rate of 20 mL per hour using a spray nozzle. The deposition took 45 minutes at the chosen temperature. The nitrogen flow was maintained until the furnace achieved normal operating temperature. After that, the product was weighed and kept in an airtight container for analysis purpose.

2.2 Preparation of MWCNTs filled Carbon Fiber Reinforced Epoxy Hybrid Nano Composite

Hybrid Nano Composite materials prepared by mechanical stirring and ultra-sonication process time are maintained constant for weight percentage of MWCNTs prepared from pine oil addition. In order to understand the effect of MWCNTs addition under the constant dispersion processing time (Mechanical stirring for 45 minutes and Ultra sonication for 45 minutes) is followed. Pre-calculated amount of MWCNTs and epoxy Diglycidal Ether of bisphenol-A (DGEBA) resin is taken and mixed together. Before that the epoxy resin is pre heated to lower the viscosity and to enable better wetting of the particles. As-grown MWCNTs mixture and resin matrix are mixed using mechanical stirrer for 45 minutes for initial mixing and under high intensity ultra-sonicator for 45 minutes. To reduce the chances of voids, the MWCNTs dispersed resin is kept under vacuum for 60 minutes. Once bubbles are trapped, required amount of hardner Triethylenetetramine (TETA) is added and manually mixed for 10 minutes.

2.3 Preparation of Composite Laminates

Composite laminates were prepared by hand layup technique. The stacking procedure consists of placing resin system (epoxy + hardener + MWCNTs) impregnated fabrics one above the other by hand layup process (8plies). To ensure the uniform thickness of the sample, a spacer of size 3mm was used. Along with release agent the mould plates were sprayed. The whole assembly was reserved in a hydraulic press and a temperature of 100°C was applied for 2 hours and the whole setup was cooled gradually to room temperature and permitted to cure for a day in order to diminish the thermal residual strains. The MWCNTs contents were varied as 0.0 % to 0.4 wt% based on the weight of the matrix and the influence of MWCNTs weight fraction on act of composite was estimated.

2.4 Characterization

Morphological structure of as-grown Multi-walled carbon nanotube characterized by SEM and HR-TEM & RAMAN analysis. Thermal properties of MWCNTs unfilled and MWCNTs filled carbon fiber reinforced epoxy hybrid nano composites were attained by acting thermo gravimetric analysis (TGA). Water absorption & Chemical resistance tests using (ASTM D570) and (ASTM 543-95) methods was employed respectively for hybrid nano composite material.

3. RESULT AND DISCUSSION

3.1 Optimization of Temperature for Maximum Yield of MWNTs and its Characterization

The effect of temperature on the yield of MWNTs from natural precursor of Pine oil at a feed rate of 20 mL per hour over Fe-Co-Mo catalysts supported on Silica is studied. In this present study, the low yield of carbon deposit was produced at 550 °C. Noticeably high yield of carbon deposit was observed for the reaction temperature at 650 °C and further increase in temperature to 750 °C results in decrease in the yield. From figure 1 the well growth of MWNTs with diameter in the range of 20-40 nm was reported using SEM. Figure 2 shown the well crystalline graphitic layers of MWNTs grown at 650 °C are also reported using HR-TEM. The inner and outer diameter of MWNTs synthesized is in the range of 10-12 and 16-22 nm respectively.

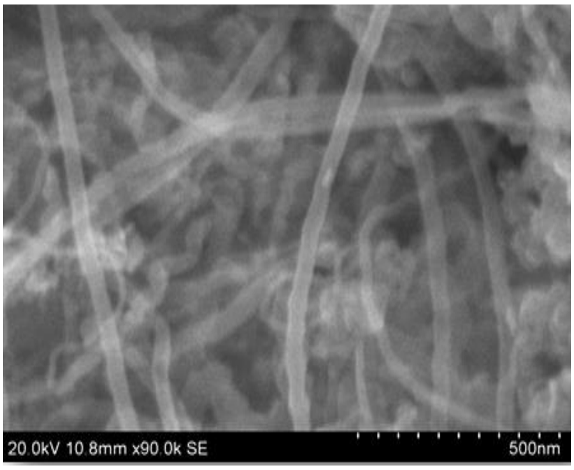

Fig. 1: SEM image of MWNTs grown at 650°C

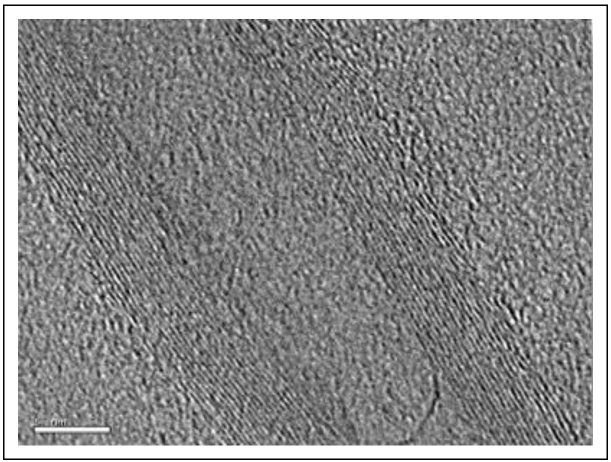

Fig. 2 HR-TEM image of MWNTs grown at 650°C

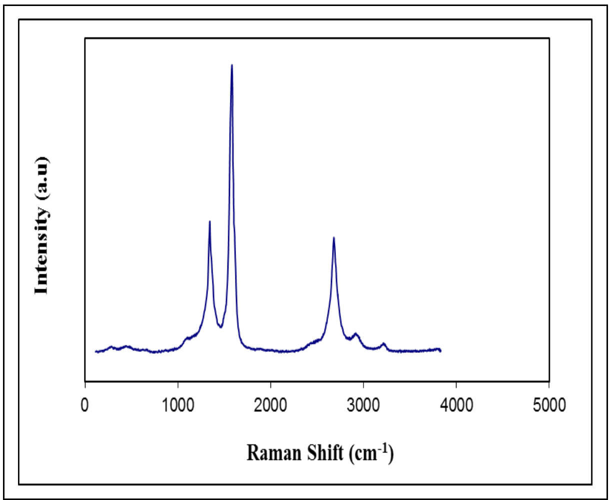

Fig. 3: Raman Spectra of MWNTs grown at 650 °C

Figure 3 shown the Raman spectrum of as-grown MWCNTs synthesized using Pine oil at 650 °C the D and G peaks are observed at 1346 cm^{-1} and 1592 cm^{-1} respectively for the CNTs prepared at 650 °C. The I_G/I_D ratio calculated from the peak area is 1.9 this high value indicated the well graphitization of the MWCNTs synthesized. Among the chosen experimental temperatures, the highest I_G/I_D ratio is observed for 650 °C. This indicates the highest quality of CNTs formed at 650 °C.

3.2 Investigation of Mechanical Properties of MWCNTs Filled Carbon Fiber Reinforced Epoxy Hybrid Nano Composite

The effects of MWCNT loading on mechanical characteristics such as tensile strength, tensile modulus, flexural strength, and flexural modulus of unfilled and MWCNTs filled carbon fibre reinforced epoxy hybrid Nanocomposites are studied in this section of the research.

3.3 Effect of MWCNTs Loading on Tensile Properties

Unfilled carbon fiber reinforced composite tensile strength & modulus values are 153.8 MPa and 5.82 GPa respectively shown in figure 4 & 5. It is proved that the properties are increasing up to 0.2 wt % of MWCNTs prepared from Pine oil and reached the highest values of 346 MPa and 9.50 GPa respectively, then the tensile properties decreases as MWCNTs which further increased up to 0.4 wt %.

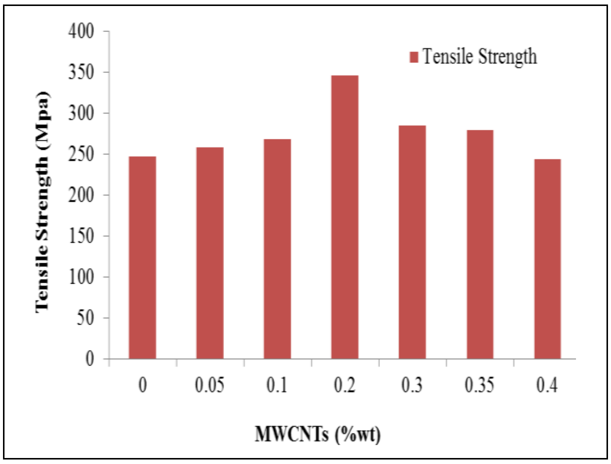

Fig. 4 Tensile Strengths for Different wt % of MWCNTs Derived from Pine Oil for MWNTs Nano Composites

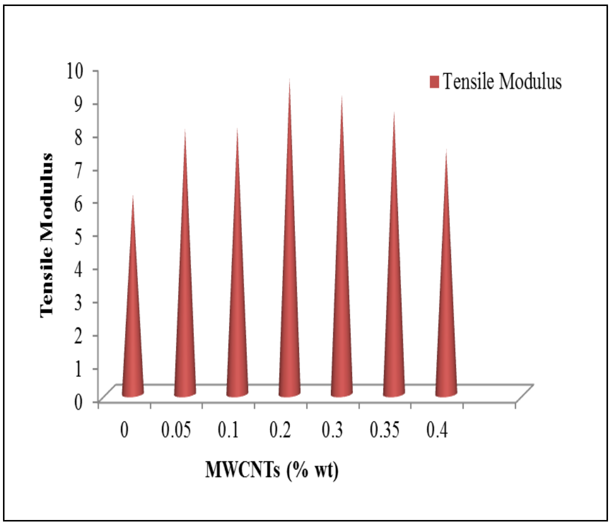

Fig.5 Tensile Modulus for Different wt % of MWCNTs Derived from Pine Oil for MWNTs Nano Composites

3.4 Effect of MWCNTs Loading on Flexural Properties

Unfilled carbon reinforced epoxy composite, flexural strength and modulus values are observed as 340.5 MPa and 25.74 GPa its observed in figure 6 & 7.

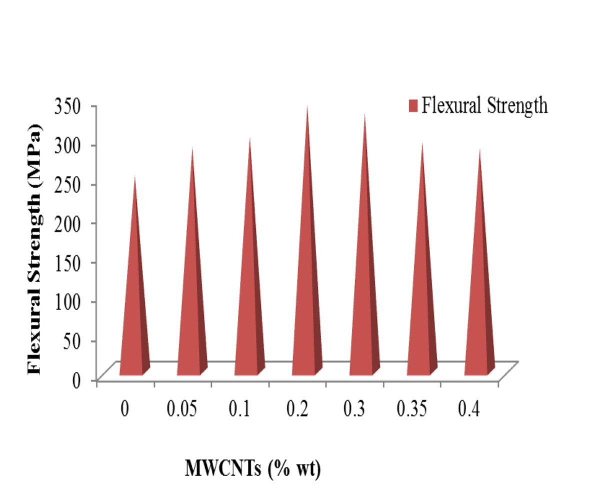

Fig.6 flexural Strengths for Different wt% of MWCNTs Derived from Pine Oil for MWNTs Nano Composite

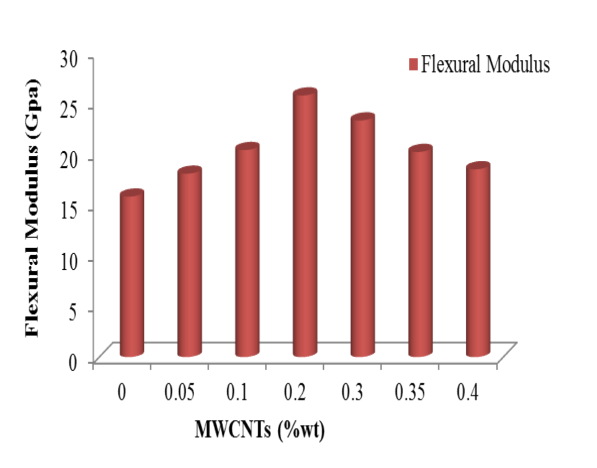

Fig. 7: Flexural Modulus for Different wt % of MWCNTs Derived from Pine Oil for MWNTs Nano Composites

It can be seen that the flexural strength and flexural modulus of MWCNTs filled carbon fiber reinforced epoxy hybrid nano composites are higher than that of unfilled EP/CF composites irrespective of the weight fractions of MWCNTs. Duo properties are increased up to 0.2 wt% MWCNTs then the properties gradually drop as MWCNTs content increased to 0.4 wt%. Optimal values are obtained at 0.2 wt% of MWCNTs. Conducted that the enhancement in the flexural properties may be due to the improved interfacial properties responsible for transfer of stresses and elastic deformation in the presence of nano filler

3.5 Investigations of thermal properties of unfilled and MWCNTs filled carbon fiber reinforced hybrid nanocomposite

This investigative method utilizes a sensitive balance to determine weight loss of a sample through a range of temperature. During the TGA analysis time is short and the sample weight required is small. The sample weight loss is measured as a utility of temperature during the investigation. The present division deals with experimental investigations of influence of MWCNTs content on the thermal properties of the unfilled and MWCNTs filled carbon fiber reinforced epoxy hybrid nano composites are evaluated by techniques such as Thermal Gravimetric Analysis (TGA).

A of weight loss details of nano composites at 400°C, 600°C and 750 °C are specified in Table 1 It clearly revealed that the weight losses at each temperature significantly lower with increase in weight % of MWCNTs content in the hybrid nano composite. This again demonstrated that the relative thermal stability of the blends depends on the weight % of MWNTs. The table 1 also clearly reveals that the decreases the weight of MWCNTs unfilled and MWCNTs filled carbon fiber reinforced hybrid nano composites with increase of MWCNTs loading from 0 to 0.4 wt%. This reveals that the char residue of unfilled and MWCNTs filled Carbon fiber reinforced epoxy hybrid nano composites significantly increased in comparison to unfilled carbon fiber reinforced epoxy hybrid nano composites. By increasing the char residue the thermal stability is enhanced as the formation of char, hinders the diffusions of the low volatile decomposition products.

Table 1. Weight Losses of MWNTs Filled Carbon Fiber Reinforced Epoxy Hybrid Nano Composites at Various Temperatures

Name of the Sample	Loss of Weight (%)			Residue Weight %
	400°C	600°C	750°C	
A	61.35	85.37	93.94	7
B	60.05	84.80	92.12	6.3
C	56.46	77.60	85.45	15.30
D	52.00	70.20	78.18	20.82
E	41.78	51.80	64.22	38.00
F	36.78	49.80	54.10	42.90
G	26.22	35.30	43.17	56.10

The results showed that 0.4 % wt of MWCNTs filled carbon Fiber reinforced epoxy hybrid nano composites (Sample G) has given the lowest weight loss (i.e. highest char) at all the specified temperatures indicating the better resistance towards thermal aging.

Table 2. Chemical Resistance Properties of Unfilled and MWCNTs filled Carbon Fiber Reinforced Epoxy Hybrid Nano Composites with Different Weight Proportions of MWCNTs

Chemicals Name	EP/CF/MWNTs nano composites as a function of MWNTs						
	0 wt%	1 wt%	2 wt%	4 wt%	6 wt%	8 wt%	10 wt%
1N HCl	+1.46	+0.61	+0.55	+0.52	+0.68	+0.45	+0.71
10N CH_3COOH	+2.21	+1.10	+2.72	+1.18	+2.07	+2.45	+2.62
1N HNO_3	+1.52	+0.96	+0.98	+0.84	+2.10	+2.58	+3.05
NaOH g/L	+0.85	+1.17	+0.89	+0.26	+0.75	+0.91	+0.43
Na_2CO_3 g/L	+0.18	-0.61	-0.58	+0.27	+0.48	+0.63	+0.75

3.6 Chemical Resistance Behavior of Unfilled and MWCNTs filled Carbon Fiber Reinforced Epoxy Hybrid Nano Composites

Table 2 demonstrate the weight gain (+) and weight loss (-) of experimental results of the unfilled carbon fiber reinforced epoxy nano composites and MWCNTs filled carbon fiber reinforced epoxy hybrid nano composites as a function of MWCNTs weight fraction when the samples are immersed in acids, alkalis and solvents. From the results it has clearly revealed that the weight expansion is observed in all the chemical regents used. This change in weight indicates that the nano composites are swollen the chemical reagents rather than dissolving. This chemical resistance behaviour study clearly demonstrated that the nano composites can be used for handling chemicals in various engineering fields.

4. CONCLUSION

The utilization of the Fe, Co and Mo as catalytic support on Silica for the synthesis of well-graphitized multi-walled carbon nanotubes with high yield at low temperature conditions using spray pyrolysis method is reported successfully. The influence of reaction temperature on the yield and morphological studies of MWCNTs synthesized from chosen precursor have revealed that 650 °C to be the most favorable temperature for the formation well-graphitized MWCNTs with better yield.

Mechanical properties of unfilled carbon fiber reinforced epoxy nano composites and MWNTs filled carbon fiber reinforced epoxy hybrid nano composites were found that the addition of multi-walled CNTs derived from Pine Oil epoxy carbon fiber composite laminates enhanced all the mechanical properties when compared with unfilled laminates. The thermal characteristics of unfilled and MWCNTs filled Carbon fiber reinforced epoxy hybrid nano composite were studied and found that the addition of MWCNTs remarkable increases the thermal stability which has been proved with the help of Thermal Gravimetric Analysis (TGA).

The chemical resistance study clearly indicates that nanocomposites can be applied for handling chemicals in several engineering fields.

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